

STATUS REPORT No. 2

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FUNDAMENTAL STUDIES ON THE SYNTHESIS OF HEAT-RESISTANT POLYMERS

I. Introduction.

This report is an informal status report covering the period from the date of Status Report No. 1 of August 6, 1963 to November 15, 1963. Status Report No. 1 established that the formation of brick dust polymers of the poly-Schiff's-base type could be avoided by reacting polyaminoaryl compounds with polycarbonyl compounds in a melt system to obtain black conjugated polymers establishing the correctness of the concept on which the research was postulated. Studies on the deficiencies of the melt and solution processes led to the discovery of a new chemical reaction which we have termed the Schiff's-base exchange. Preliminary studies disclosed three fundamental modifications of the Schiff's-base exchange, namely, (1) the carbonyl exchange as illustrated by an aldehyde, (2) a base exchange as illustrated by an aryl amine, and (3) a bis-exchange as illustrated by two Schiff's bases to produce two different Schiff's bases. This discovery was extended successfully through preliminary experiments to include the preparation of polymeric Schiff's bases by means of reactants whose functionality was at least two. The breadth and depth of the Schiff's-base-exchange reaction and

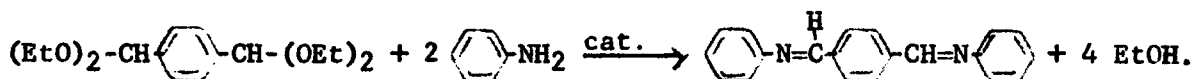
A. Aromatic Acetals Reaction with an Aromatic Amine.

1. The Reaction of a Monofunctional Aromatic Acetal with a Monofunctional Aromatic Amine.

The reaction of a monofunctional aromatic acetal with an aromatic amine was found to proceed directly through a double elimination to a Schiff's base (equation 1). This reaction was studied with and without a catalyst. The reaction conditions studied with a catalyst were one hour at 55°C; and without a catalyst for thirty minutes at 100°C. In either case a 90% yield of the Schiff's base (II) was obtained and none of the intermediate (I). A qualitative study was made of the elimination rate constants, k_1 and k_2 by a determination of the amount of alcohol liberated. It can be shown that $k_2 \cong k_1$ or $k_2 > k_1$, and so no intermediate would be isolable. It was also found that *p*-toluene sulfonic acid is a more active catalyst than zinc chloride.

2. The Reaction of a Difunctional Aromatic Acetal with a Monofunctional Amine.

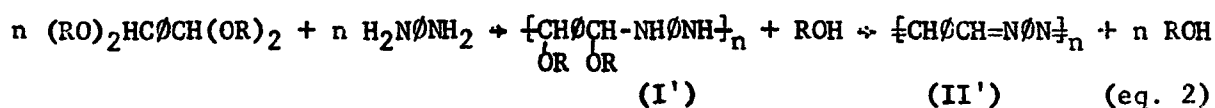
In a study similar to that of III.A.1 it was also found that the reaction of a difunctional acetal with an arylamine proceeds directly through a double elimination to a Schiff's base as illustrated by the following reaction



The yield of product in the above reaction at the time interval used was 80%. The reaction products were identified and characterized by infrared spectra and melting points.

3. Polymerization Reaction of a Difunctional Aromatic Acetal and a Difunctional Aromatic Amine.

A polymerization study was made of xylylenetetraethylether and *p*-phenylenediamine,

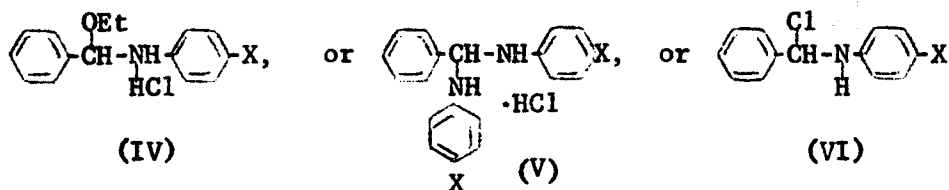
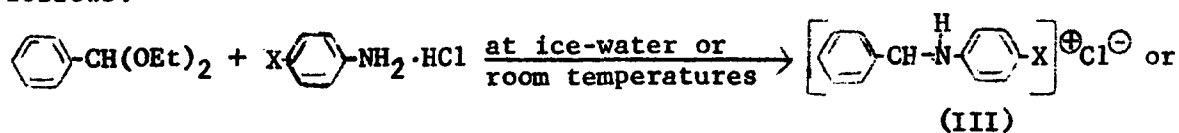


After seven minutes of reaction at 84°C, ethanol generation was detected. A complete melt of the reaction mixture was obtained at 95°C. After fifteen minutes of reaction at 100°C a dark yellow precipitate was obtained. The temperature was ultimately raised to 280°C. A low molecular weight brown solid was obtained at the completion of the reaction. This synthesis is similar in behavior to a direct condensation of a dialdehyde and diamine, and since the elimination rate constant relationships have been shown to be $k_2 \cong k_1$ or $k_2 > k_1$, no quantity of soluble and/or fusible intermediate (I') was isolatable during the course of the reaction. For this reason, a comparable study was made using aromatic amine hydrochlorides in an attempt to isolate the intermediate (I').

B. Aromatic Acetal Reaction with an Aromatic Amine Hydrochloride.

1. Monofunctional Reaction.

In an attempt to isolate the intermediates discussed above, a study was made of the reaction of acetals and amine hydrochlorides in bulk and in solution at or below room temperature. The general reaction may be written as follows:



The postulated reaction products, (III), (IV), (V), and (VI) were then neutralized with base, and Table 1 summarizes the products obtained after neutralization as a function of the substituent X.

By hydrolysis of the products formed, it is possible to explain the formation of the final compounds given in Table 1.

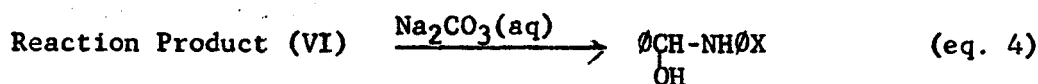
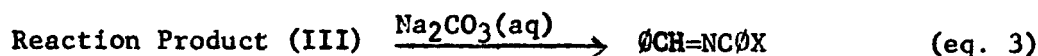
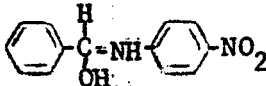


Table 1

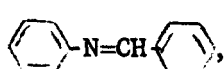
Reaction Product Obtained after Neutralization for Various X-Substituents on Aromatic Amine Hydrochloride, after Reaction with the Acetal

| X-Substituent | Neutralization Product |
|-----------------------|---|
| -H | Acetal and Aniline |
| -Cl | Schiff's Base |
| -NH ₂ ·HCl | Schiff's Base |
| -NO ₂ |  |

It was concluded by additional data obtained from alkalimetry and infrared spectra together with the data of Table 1, that in all the cases studied where reaction occurs, an adduct of the structure (III) is first formed as an intermediate in this class of reactions.

2. Difunctional Reaction.

Difunctional Aromatic Acetal and Monofunctional Amine Hydrochloride.

A study comparable to III.B.1 was made with a difunctional acetal and ring-substituted monofunctional amine hydrochlorides, thus $(\text{RO})_2\text{CH}\text{OCH}(\text{OR})_2$ plus $\text{XC}_6\text{H}_4\text{NH}_2\cdot\text{HCl}$. The products obtained after neutralization were Schiff's bases, except in the case of p-nitroaniline hydrochloride, and thus the results were similar to the results in Table 1. In addition, further confirmation of the constitution of the adducts, and their hydrolysis behavior, was obtained by the reaction of $\text{X}-\text{C}_6\text{H}_4-\text{N}=\text{CH}-\text{C}_6\text{H}_5$, in which $\text{X} = -\text{H}, -\text{Cl}, -\text{NO}_2$, , with dry hydrogen chloride gas followed by hydrolysis.

3. Polymerization Reaction.

Difunctional Aromatic Acetal with Difunctional Aromatic Amine Hydrochloride.

Preliminary polymerization studies were made both in bulk and in solution using paraphenylene diamine dihydrochloride in a system similar to that of III.B.2 above. A bulk (i.e., an undiluted melt) polymerization was run in the temperature range of 220 to 280°C under a nitrogen atmosphere, and a black polymer was obtained, which had some areas of yellow and blue coloration. In solution polymerization, a yellow to brown poly-Schiff's base of low molecular weight was obtained after neutralizing the poly-Schiff's base hydrochloride. In general, bulk polymerizations with the amine hydrochlorides produced polymers of higher molecular weight, as evidenced by color, than those obtained in solution polymerization. This confirms previous experiences with the free dialdehyde and diamine. The experimental data obtained to date indicates that it is most improbable, because of the specific rate constants involved, that the desirable intermediate can be isolated from the reaction of the acetal and either the free amine or the hydrochloride of the amine. However, the study using acetals has led to a new and previously unknown synthesis of Schiff's bases (equation 1) which was shown not only to be widely applicable as a new synthetic method (Table 1) for non-polymeric compounds, but that it is applicable also to the preparation of polymers.

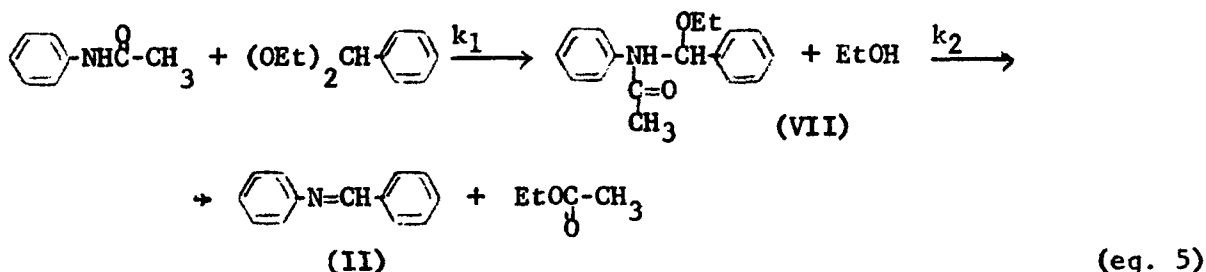
Further and different syntheses were then made in the attempts to control the general Schiff's base reaction to isolate a soluble intermediate. It is most interesting that these new approaches have also led to new discoveries. The newest approach was to react the aromatic acetal with a N-substituted amine, wherein the substituent group could possibly undergo elimination as shown in Items C and D below.

In all these cases, as in the cases of the Schiff's base exchange, the reaction of acetals with amines or their salts, there exists no data in the technical literature on which to base an understanding of a polymerization reaction. Accordingly, as must be done in such cases, it has been necessary to study prototype reactions with ordinary low molecular weight organic compounds and to derive thereby a mechanism which can be proposed for the polymerization system. It is rational to believe that, if a reaction "goes" or "does not go" in a simple system, or that a specific rate constant, k_1 , is approximately equal to or greater than k_2 in a series of reactions, the same limitations will be found for the same type reaction when it is used to prepare polymers. In all the new systems investigated, we have therefore first evaluated the proposed reaction with simple organic compounds in simple non-polymeric systems.

C. Reaction of an Aromatic Acetal with an N-Substituted Aromatic Amine.

1. Monofunctional Reaction.

The reaction of a N-substituted amine with an acetal was studied in which the N-substitution consisted of an acyl group, specifically $\text{CH}_3\text{CO}-$. Equations for the proposed reactions may be written as



The reaction temperature required to obtain (II) yield was found to be in the range of 150-220°C. At the start of the reaction, however, the distillate was essentially EtOH. As the reaction proceeded, the quantity of EtOH in the distillate became progressively less and that of EtOCOCH_3 in the distillate gradually increased. From the data obtained two most

important conclusions can be made, namely, that

a) $k_1 > k_2$ and

b) the existence of an intermediate which is soluble and fusible in polymerization reactions is highly probable.

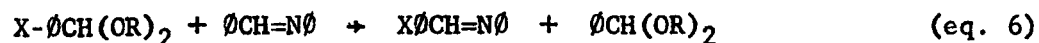
2. Polymerization Studies with Difunctional Reagents.

Polymerization studies were made with difunctional compounds both in bulk and in solution using xyridenetetraethylether and p-(N-diacyl)phenylene diamine. In bulk polymerization without a catalyst a reddish-brown polymer was obtained after twenty-four hours at 220°C, which after additional heating for approximately one hour at 300°C, resulted in a high molecular weight black polymer. When p-toluene sulfonic acid was used as a catalyst, a high molecular weight black polymer was obtained directly without thermal post-treatment. A high molecular weight black polymer may be obtained, therefore, by either a catalyzed or an uncatalyzed system by this new reaction.

Solution polymerizations were run also in N-methyl pyrrolidone with and without a catalyst. It was found that a high molecular weight polymer could be obtained in five hours at 220°C without a catalyst. With an acidic catalyst, an alcohol-soluble yellow polymer was obtained after six hours at 150°C, which after isolation and standing overnight in air, became a black, high molecular weight polymer insoluble in ordinary organic solvents. Solution polymerization of diacetals and n-substituted amines thus offers a new and most interesting route to high molecular weight poly-Schiff's-base polymers. This led to experimentation involving the reaction of acetals with Schiff's bases as given in the next item, III.D.

D. Acetal-Schiff's-Base Exchange.

This postulated reaction which may be written as

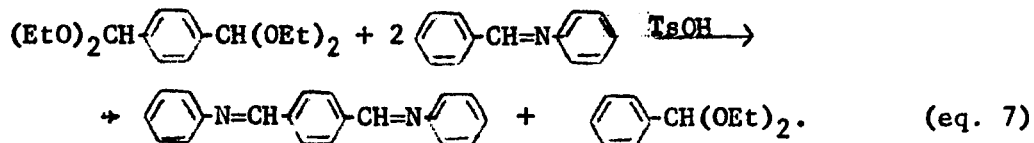


also is not known in the literature. It was evaluated using an aromatic

diacetal with aromatic Schiff's bases of mono- and diamines.

1. With Monofunctional Base.

The exchange reaction of an aromatic diacetal with a Schiff's base was studied with a mono-Schiff's base for which the following reaction can be written:



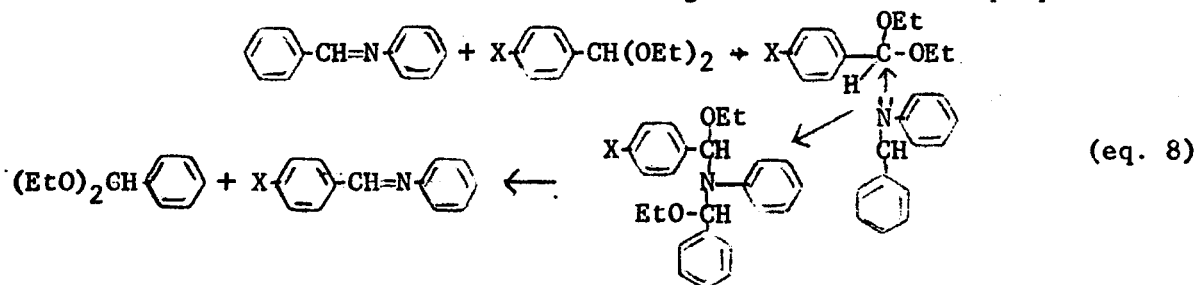
Under the reaction conditions of four hours at 200-220°C at atmospheric pressure, a 60% yield was obtained. The resulting products were identified and characterized by melting point and infrared analysis, confirming the postulated reaction.

2. Polymerization.

This was investigated by the reaction of the difunctional acetal above with a Schiff's base of a difunctional amine, $\text{OCH}=\text{N}\text{N}=\text{CH}\text{O}$. Bulk polymerizations were run at a) reduced pressure and b) atmospheric pressure. Under both conditions a high molecular weight black polymer was obtained, passing through a viscous and soluble stage. The polymer obtained at reduced pressure appeared to be of higher molecular weight than the polymer prepared at atmospheric pressure.

3. Mechanism of the Acetal-Schiff's-Base-Exchange Reaction.

A study was made of the mechanism of this new acetal exchange reaction with Schiff's bases for which the following mechanism is now proposed:



The exchange reaction was studied with three types of "X" substituents; -H, -Cl, and -NO₂, with and without a catalyst. The reaction temperature

was 120°C and the catalyst used was p-toluene sulfonic acid. The reaction products were identified by infrared spectra and Table 2 summarizes the results in terms of whether or not a reaction occurs.

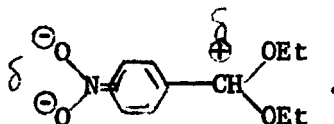
Table 2

Effect of Substituent on Acetal Reaction
With and Without a Catalyst

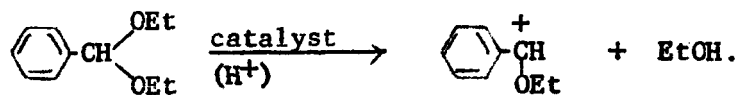
| Substituent "X" | No Catalyst | Catalyst |
|--------------------|----------------|----------|
| H | (-) | (+) |
| Cl | (-) | (+) |
| NO ₂ | (+) | (+) |

+ indicates reaction took place
- indicates no reaction

If X is a highly electron-withdrawing substituent, the positive character of the attaching carbon of the acetal is enhanced, thus:



In such a case a catalyst is not always required to promote the reaction. Without a highly electron-withdrawing substituent on the acetal, a catalyst is needed to promote the reaction, and probably functions as follows:



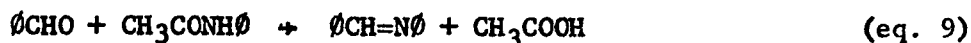
Electropositive species may be prepared, therefore, by either incorporating an electron-withdrawing group on the ring, or protonation with a catalyst. Then, the unpaired electrons on the nitrogen of the Schiff's base attacks the positive species as shown in the proposed mechanism.

This data supports, in part, the proposed mechanism, and can account for the existence of the intermediate which is soluble and fusible in the polymerization reaction. Further, fundamental information of this kind will be most useful and important in the studies concerned with the semi-

conductor properties of the polymers.

IV. New Schiff's Base Syntheses Using Aromatic Aldehyde and N-Substituted Aryl Amines.

The success of the synthesis of Schiff's bases from the acetals and acetanilides (equation 5) prompted an evaluation of the reaction using the aldehyde according to the reaction



which was evaluated for both monofunctional and polyfunctional systems, even though little hope was held that it would succeed.

A. Uncatalyzed Systems.

1. Monofunctional System.

This reaction of benzaldehyde with acetanilide was tried at 180-220°C for forty-eight hours under nitrogen gas without a catalyst. Only a trace amount of CH_3COOH was detected indicating a reluctance for this reaction to occur. The major portion of the product recovered was starting materials.

2. Polyfunctional System.

This type reaction was then repeated using difunctional compounds. A molar mixture of terephthalaldehyde and n-diacyl p-phenylenediamine was heated at 200°C for thirty-five hours under N_2 gas with no catalyst. The reaction product was a brown insoluble polymeric solid, whose IR spectra did not conform to that of a typical polymeric Schiff's base and therefore was not investigated further.

B. Catalyzed Systems.

1. Monofunctional System.

The reaction of IV.A.1 was repeated using toluene sulfonic acid as a catalyst and a small yield of a solid yellow product, m.p. 137°C, which is not benzyl aniline, OCH=NO , (equation 9), and therefore the reaction was not investigated further.

2. Polyfunctional System.

The reaction of IV.A.2 was repeated with catalyst and a polymeric product of a darker brown color than that obtained in the uncatalyzed system (IV.A.2) was obtained. However, the IR spectra is not that of a typical poly-Schiff's base, though there were indication of a few $-\overset{\text{H}}{\text{C}}=\text{N}\phi-$ bands. In general, it may be concluded that the reaction given by equation 9 is not satisfactory for the preparation of either simple or polymeric Schiff's bases.

V. Intermediates Prepared and in Preparation.

It was pointed out in Progress Report No. 1 that the project has required the syntheses of a large number of intermediates; and a number of them have already been reported. This phase of the work has continued with the synthesis of some new compounds as well as improvements in the syntheses of some of the compounds previously reported. They are:

A. Quinone Schiff's Base Derivatives.

1. Quinone Dianil, m.p. = 180-181°C.

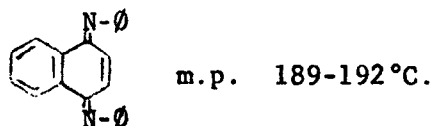
This monomer was prepared by mild oxidation of N,N'-p-phenylenediamine with quinone as previously reported and has now been purified to satisfactory standards for use in polymerization studies.

Analysis: Theoretical: C, 83.72; H, 5.43; N, 10.85.

Found: C, 83.83; H, 5.47; N, 10.72.

2. Naphthaquinone Dianil.

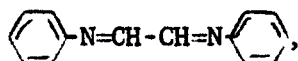
The Schiff's base of naphthaquinone and aniline was prepared by the direct condensation of 1,4-naphthaquinone with aniline by the new azeotropic method:



It will be purified to suitable standards for future use.

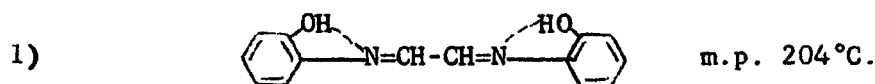
B. Glyoxal Schiff's-Base Derivatives.

Attempts to prepare the unsubstituted monomer,



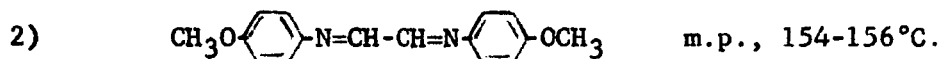
were unsuccessful.

Experiments involving direct condensation of aniline with glyoxal repeatedly resulted in polymeric material. Two substituted compounds of suitable purity, however, have now been successfully prepared using high dilution techniques. These compounds were



Analysis: Theoretical: C, 70.00; H, 5.00; N, 11.67.

Found: C, 70.31; H, 5.12; N, 11.48.



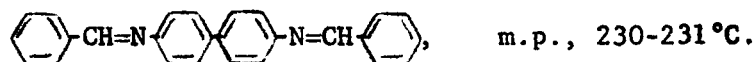
Analysis: Theoretical: C, 86.6; H, 7.80; N, 5.60.

Found: C, 86.1; H, 8.41; N, 5.79.

These results show that compounds of this general type may be prepared by the introduction of appropriate substituents on the benzene ring of the aniline.

C. Benzidine-Type Monomer.

The Schiff's base of benzidine and benzaldehyde was prepared by direct condensation in absolute benzene by the new azeotropic method:



Analysis: Theoretical: C, 86.6; H, 7.80; N, 5.60.

Found: C, 86.1; H, 8.41; N, 5.79.

Further purification of this monomer is in progress.

D. Pyridine Schiff's-Base Derivatives.

The Schiff's base of 2-amino pyridine and terephthalaldehyde was prepared by direct condensation in absolute benzene, by the new azeotropic method.



Analysis: Theoretical: C, 75.52; H, 4.90; N, 19.58.

Found: C, 75.90; H, 5.33; N, 18.82.

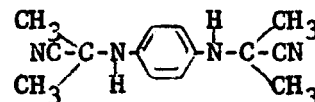
This type of a monomer should supply its own base catalysis in a polymerization reaction, and if this proves to be an important consideration, additional monomers of the type can be made easily.

E. Ketone Dianils.

A typical ketone dianil is, $\text{CH}_3-\text{C}(\text{CH}_3)=\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{C}(\text{CH}_3)_2$. This class of com-

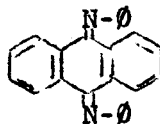
pounds is desired for investigation to assure broad coverage of the Schiff's-base-exchange reaction.

Three methods were used to prepare this compound, using techniques described in the chemical and patent literature¹⁻³ for the preparation of ketone monoanil. The first method tried was the condensation of acetone and *p*-phenylene diamine (ref. 1). The second method tried was the reaction of 2,2-dimethoxypropane with *p*-phenylene-diamine (ref. 2). The third method attempted was the preparation of cyano intermediate



which would subsequently produce the ketone dianil by elimination of HCN (ref. 3). None of these methods was successful and starting material was recovered in each case. The most promising of the methods appeared to be the reaction of the acetal with the primary amine (ref. 2) but at this time, it has not been explored further.

F. Anthraquinone Dianil.

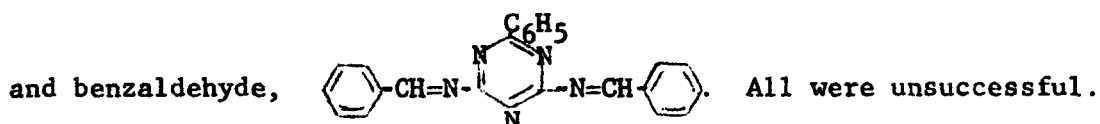


1. U.S. Patent 2,218,587, October 22, 1940.
2. Berichte 29, 2932 (1896).
3. Biochimia, 22, 183 (1957).

Three attempts were made to prepare this compound, without success. First, a direct condensation with aniline in benzene was tried. This resulted in the recovery of starting material. Then a catalytic system was studied and the reaction attempted at the boiling point of xylene; again starting material was recovered. Finally, an organic catalyst was substituted for the inorganic catalyst, and this too was unsuccessful and starting material was recovered.

G. Triazine-Type Schiff's Base Monomers.

Four attempts were made to prepare the Schiff's base of benzoguanamine



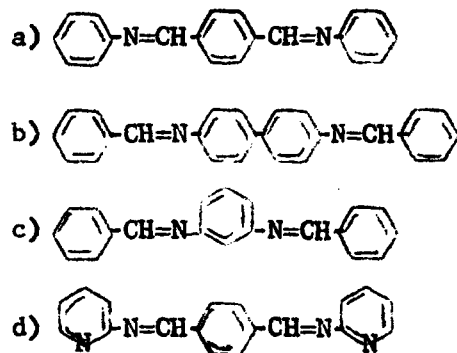
First, a direct condensation of benzaldehyde with benzoguanamine was attempted using a zinc chloride catalyst and benzene solvent. Then *p*-toluene sulfonic acid was used as a catalyst and xylene for the solvent. A dehydrating agent was then tried (Ac_2O) to assist in removal of the H_2O of reaction. Next a reaction of benzaldehyde with benzoguanamine hydrochloride was attempted. Finally, a melt reaction of *o*-chloro benzaldehyde and benzoguanamine was tried. In all cases, the products obtained were either polymeric or starting materials.

H. Improved Process for Preparing Monomers.

A new procedure previously reported as under study is now being used to prepare monomers in larger quantities with near quantitative yields.

The procedure used involves the removal of H_2O during the course of the reaction by azeotropic distillation and trapping the condensed water in a Dean-Stark trap. Large batches of the following monomers, a to d, were prepared by this technique and purified to a high degree of purity for the detailed polymerization studies soon to be undertaken.

Monomers Proposed in High Purity.



I. Transamidation.

The Schiff's base exchange reactions are related to transamidation. Limited, preliminary experimentation has been done with the expectation that knowledge of the transamidation mechanism will be useful in interpreting the data of the Schiff's base reaction.

The work of Klamann⁴ on the transamidation of benzamide with aniline hydrochloride was repeated. The reaction of benzamide with aniline in the absence of a catalyst gave benzanilide in up to 80% yield.

The reaction of benzamide with p-chloroaniline was also successful and gave 4'-chlorobenzanilide in about 50% yield. Both of these reactions were carried out by mixing the reagents and heating in the absence of oxygen to 180-200°C.

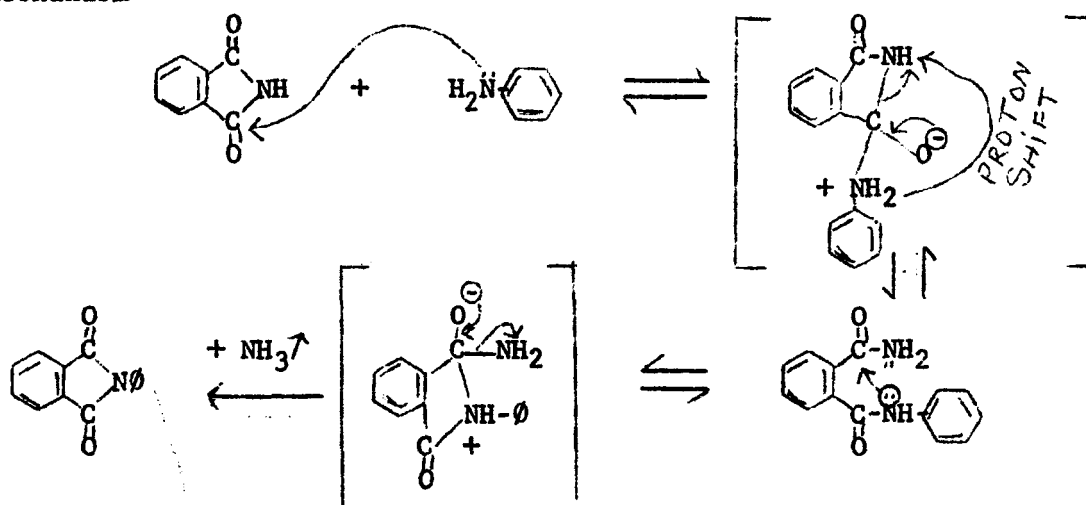
The transamidation of benzamide with p-nitro-aniline was also tried and was unsuccessful even with a catalyst. Both a Lewis acid, zinc chloride, and a proton acid, HCl were used.

A persistent problem in all of these cases, but especially in the case of the nitro-aniline reaction, has been the dehydration of benzamide to benzonitrile. Perhaps this could be overcome by using N-methylbenzamides.

Klamann's work⁴ also included a transimidation reaction with phthalimide and aniline hydrochloride. This reaction was repeated using aniline

4. D. Klamann, Monatsh. fur Chem., 84, 925 (1923).

rather than aniline hydrochloride and phthalanil was obtained in about 80% yield. It is likely that this reaction goes through the following mechanism



which is related somewhat to the mechanism we propose for the Schiff's base exchange.

V. Summary and Conclusions.

The investigations performed between the period of August 6, 1963 and November 15, 1963 have augmented the results reported on August 6, 1963. A number of other new syntheses for Schiff's bases were discovered, and augmented NASA possible patent application structure from about thirteen previously reported to seventeen, the increase resulting from four new acetal reactions discovered, namely:

14. Acetals with Aromatic Amines;
15. Acetals with Aromatic Amine Salts;
16. Acetals with N-Acyl Aromatic Amines;
17. Acetals with Non-Polymeric Schiff's Bases.

These reactions were proven first in non-polymeric systems and they were shown to be applicable to the synthesis of the type of polymers proposed under this project. In the studies completed, a preliminary understanding of the mechanism was derived from some kinetic experiments which indicate

that some derivatives of the aldehyde and some derivatives of the amines favor the existence of intermediates which facilitate the production of the desired polymers. An attempt was made to extend this reasoning to the reaction of the aldehyde and an acyl amide without success. It is our belief that the permutations possible for syntheses of Schiff's bases have been bracketed and accordingly, NASA's patent position has been adequately protected. Some preliminary work on non-polymeric systems necessary to back up our knowledge on the polymeric systems is still in progress and should be completed by December 1, 1963, after which concentrated effort can be given to detailed polymerization studies.

The research schedule for the next period is given in Item VI.

VI. Research Planned for the Period November 15, 1963 to January 31, 1963.

The research plan remains substantially unchanged from that presented in Status Report No. 1 except for items which have been completed. With these revisions, it is planned to continue to make as much progress as possible on the following plan, with no hope for its completion within the present period of the grant:

- 1) Begin the detailed polymerization studies involving (a) the contrast of the various methods of producing the conjugated polymers, (b) the kinetics and mechanism of the polymerization reaction, (c) the establishment of appropriate methods for determining the molecular weight of the polymers obtained;

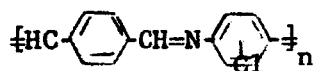
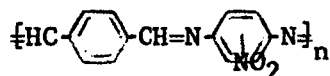
- 2) Synthesize pure monomers and intermediates required for research on the project;

- 3) Undertake initial studies with one or more of the conjugated polymers to determine the limit of the degree of polymerization at which the polymer is still soluble, and/or fusible, and at which stage it can still be fabricated. Then extend the study to solid phase polymerization of

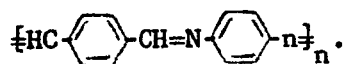
these intermediates and establish the conditions required to obtain maximum physical properties;

4) Start to explore the semiconductor properties of the polymers. The conjugated polymers of this project are not only highly heat-resistant but also organic semiconductors, a property which we anticipated and which now has been confirmed.

Our concepts include the introduction of electron-withdrawing and electron-donating groups on the segments of the polymer. Accordingly, we will attempt the synthesis of a few such substituted polymers to compare their semiconductor properties with the unsubstituted parent polymers. Most probably, we will attempt the synthesis of one or both of the following polymers:



for comparison with the parent polymer,



Some of the studies already made on non-polymeric Schiff's bases reaction with X-substituent groups will be applicable and most useful in this particular phase of this research.